



PATENT APPLICATION

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Title:

Conducting Polymer Nanofiber Sensors

SPECIFICATION

Statement of Government Interest

The invention was made with Government support under contract No. F04701-00-C-0009 by the Department of the Air Force. The Government has certain rights in the invention.

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Reference to Related Application

The present application is related to applicant's  
copending application entitled "Synthetic Method for Conducting  
Polymer Nanofibers", S/N: xx/xxx,xxx, filed yy/yy/yy, by the  
same inventors.

Field of the Invention

The invention relates to the field of nanostructured  
polymers. More particularly, the present invention is related  
to methods of manufacture of conducting polymer nanofibers and  
sensors made of conducting polymer nanofibers.

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## Background of the Invention

Since the discovery that conjugated polymers can be made to conduct electricity through doping, research has been extended in the field of conducting polymer films. Polymers have been made as conducting links of organic monomers having defined chemical structures. Polyaniline can be made as a conducting polymer of aniline monomers. Polyaniline is a unique conjugated polymer in that polyaniline can be tailored for specific applications through a non-redox acid and base doping process. Polyaniline has been studied for electronic and optical applications, such as lightweight battery electrodes, electromagnetic shielding devices, anticorrosion coatings, and sensors. Unlike other conjugated polymers, polyaniline has a simple and reversible acid doping and base dedoping chemistry enabling control over properties of the polyaniline, such as density, solubility, conductivity, and optical absorption. One-dimensional polyaniline nanostructures, including nanowires, nanorods, and nanotubes possess low-dimensional sizes and organic conduction. The electrically conductive form of polyaniline is known as emeraldine having an oxidation state which, when doped with an acid, protonates the imine nitrogens on the polymer backbone and induces charge carriers. The conductivity of polyaniline increases with doping from the undoped insulating emeraldine base form,  $\sigma < 10^{-10}$  S/cm, to the fully doped, conducting emeraldine salt form,  $\sigma > 1$  S/cm. Dopants can be added in any desired quantity until all imine nitrogens, that is half of the total nitrogens, are doped, by

1 controlling the pH of the dopant acid solution. Dopants can be  
2 removed by interacting the emeraldine salt form with common  
3 bases such as ammonium hydroxide.

4  
5 Conducting polymers can be used in sensors having optical,  
6 electrochemical and conducting properties. Conducting polymers  
7 are unique by changing properties when chemically treated with  
8 oxidizing or reducing agents. After chemical treatment with  
9 protonating, deprotonating, oxidizing or reducing agents, the  
10 conducting polymer polyaniline can reversibly change from an  
11 initially electrically insulating state to a conducting state.  
12 This transition can be used in such applications as optical  
13 sensors, chemical sensors, and biosensors. Conducting polymers  
14 include polyaniline, polypyrrole, polythiophene, and their  
15 derivatives. Polyaniline is a conducting polymer that is  
16 environmentally stable and can react with chemical species at  
17 room temperature. As such, polyaniline may be suitable for gas  
18 sensing applications using processes that create a uniform thin  
19 film of the polyaniline. This thin film may then react with  
20 protonating and deprotonating agents to create a conduction  
21 pathway that can easily be measured.

22  
23 The conductivity depends on both the ability to transport  
24 charge carriers along the polymer backbone and the ability of  
25 the carriers to hop between polymer chains through interpolymer  
26 conduction. Any interactions with polyaniline that will alter  
27 either of these conduction processes will affect the overall  
28 conductivity. This is the underlying chemical property enabling

1 polyaniline to be used as the selective layer in a chemical  
2 vapor sensor, such as, a resistance detector generally known as  
3 a chemiresistor. Due to room temperature sensitivity, the ease  
4 of deposition onto a wide variety of sensor substrates and due  
5 to the various structures, conducting polymers are potential  
6 materials for sensor applications. A polymer chemiresistor  
7 would typically consist of a substrate, electrodes, and a  
8 conducting polymer selective thin film. Changes in conductivity  
9 of the polymer film upon exposure to chemical vapors can be  
10 readily monitored with an ohmmeter or electrometer. Polyaniline  
11 sensor research has focused on changing the polymer structure  
12 to facilitate interaction between vapor molecules and the  
13 polymer either by modifying the polymer backbone or the  
14 interchain connections. However, poor diffusion can readily  
15 outweigh any improvements made to the polymer chains because  
16 most of the material other than the limited number of surface  
17 sites, is not available for interacting with a chemical vapor,  
18 thus degrading sensitivity. One way to enhance diffusion is to  
19 reduce film thickness, such as producing monolayers of  
20 conventional polymer materials, which leads to a trade-off  
21 between sensitivity and robustness. Coating polyaniline on  
22 porous substrates can increase the surface area, but the  
23 chemistry and physics involving polymer support and polymer  
24 electrode interfaces is not well defined for practical use.

25  
26 Nanostructured polyaniline, such as nanowires, nanofibers,  
27 nanotubes, and nanorods may have sufficiently high surface area  
28 and faster diffusion rates of gas molecules into the

1 nanostructures for use as chemical sensors with increased  
2 sensitivity, as compared to bulk polyaniline. For example, the  
3 surface area per unit mass  $S_A$  of polyaniline nanofibers  
4 increases geometrically as the diameters  $d$  of the nanofibers  
5 decrease, that is  $S_A \sim 1/d$ . Even when the thickness of an ultra-  
6 thin film is the same as the diameters of the nanofibers, the  
7 fibers may outperform a thin film because the fibers have  
8 higher surface-to-volume ratios due to their cylindrical  
9 morphology. The small diameter of the nanofibers, for example  
10 less than 500 nm, coupled with the possibility of gas  
11 approaching from all sides should give sensors with improved  
12 performance. Despite the high surface area and porosity  
13 associated with nanostructures, nanostructured polyaniline has  
14 not been used as chemical sensors. This is due to uncertain  
15 nanostructure characterization as well as the lack of reliable  
16 methods to make high quality polyaniline nanofibers, and  
17 reliable methods to coat surfaces with polyaniline nanofibers.  
18 No practical nanostructured conducting polymer sensors are  
19 available due to the lack of reliable methods for making high  
20 quality conducting polymer nanostructures in bulk quantities  
21 and the unknown properties of nanofiber characterization.

22  
23       Syntheses of polyaniline nanostructures have been carried  
24 out both chemically and electrochemically by polymerizing the  
25 aniline monomers with the aid of either a hard template or a  
26 soft template. Examples of hard templates include zeolite  
27 channels, track-etched polycarbonate, nanoporous membranes, and  
28 anodized alumina. Examples of soft templates for self-assembly

1 of functional polymers include surfactants, polyelectrolytes,  
2 or complex organic dopants, such as micelles, liquid crystals,  
3 thiolated cyclodextrins, and polyacids, that may be capable of  
4 directing the growth of polyaniline one-dimensional  
5 nanostructures with diameters smaller than 500 nm. Adding  
6 structural directing molecules such as surfactants or  
7 polyelectrolytes to the chemical polymerization bath is one way  
8 to obtain polyaniline nanostructures. When organic dopants with  
9 surfactant functionalities are used, emulsions or micelles can  
10 be formed leading to microtube, microfiber, or microrod  
11 structures. However, when polyaniline nanostructures with  
12 diameters of less than 500 nm are desired, then very complex  
13 dopants with bulky side groups are needed, such as sulfonated  
14 naphthalene derivatives, fullerenes, or dendrimers.

15  
16       The formation of polyaniline nanostructures  
17 disadvantageously relies either on guidance from hard templates  
18 or self-assembled soft templates. These templates  
19 disadvantageously use complex synthetic conditions that require  
20 the removal of such templates and hence provide low yields and  
21 with poor reproducibility. Chemical methods of making  
22 polyaniline nanostructures, such as nanotubes, nanofibers,  
23 nanowires, and nanorods, disadvantageously require specific  
24 structure-directing template materials added into or applied to  
25 the polymerization bath. The synthetic conditions  
26 disadvantageously have to be carefully designed to accommodate  
27 formation and purification to obtain pure polyaniline  
28 nanostructures. These template methods are disadvantageously

1 dependent on either a template or a specific complex chemical  
2 reagent, and post-synthetic treatments are needed to remove the  
3 reagent from the byproducts in order to recover pure  
4 nanostructured polyaniline. Therefore, developing synthetic  
5 production methods that do not rely on templates, structural  
6 directing molecules, or specific dopants is desirable,  
7 especially for scaling up to produce large quantities of  
8 nanostructured materials suitable for mass usage in chemical  
9 sensors.

10  
11       Electrochemical polymerization and physical methods, such  
12 as electrospinning and mechanical stretching can produce  
13 conducting polymer nanofibers without templates, but these  
14 conducting polymer nanofiber materials can only be made on  
15 carefully prepared surfaces offering limited production  
16 scaling. Electrochemical synthesis of polyaniline has indicated  
17 that some nanofibers form naturally on a synthesis surface  
18 while the underlayer is much more compact with microfiber  
19 polymers. For the production of polyaniline nanofiber sensors  
20 in quantity, there exists a need for a practical bulk synthetic  
21 method. Despite the variety of current synthetic methods  
22 available to produce polyaniline nanostructures, there is a  
23 need for a practical synthetic method capable of making pure,  
24 uniform, and template-free polyaniline nanostructures with  
25 predetermined small diameters and in bulk quantities. Current  
26 synthetic methods are not useful in mass production of ultra-  
27 small, low-dimensional structures, such as sensors, using  
28 conductive polymer nanofibers of polyaniline. These and other



1 disadvantages are solved or reduced using the present  
2 invention.

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Summary of the Invention

An object of the invention is to provide a method for forming a conductive polymer.

Another object of the invention is to provide a method for forming conductive polymer nanofibers.

Another object of the invention is to provide a method for forming conductive polymer nanofibers with predetermined diameters.

Yet another object of the invention is to provide a method for forming conductive polymer polyaniline nanofibers.

A further object of the invention is to provide a method for forming and purifying conductive polymer polyaniline nanofibers in a polymerization bath suitable for production scaling in bulk quantities.

Still another object of the invention is to provide chemical sensors made from conductive polymer polyaniline nanofibers.

Yet a further object of the invention is to provide chemical sensors made from conductive polymer polyaniline nanofibers having strong adherence to conducting terminals.

1 The invention is directed towards methods for producing  
2 conducting polymer nanofibers and chemical sensors made of  
3 conducting polymer nanofibers. In a preferred form, conducting  
4 polyaniline nanofibers are produced in a polymerization bath,  
5 suitable for batch bulk production and suitable for making a  
6 variety of chemical sensors. Polyaniline nanofibers can be  
7 doped with an acid and dedoped using a base, in a reversible  
8 chemical process. Discovery is made that nanostructured  
9 polyaniline has greater sensitivity and faster chemical time  
10 responses than the bulk form due to higher effective surface  
11 areas and shorter penetration diffusion depths for gas  
12 molecules. Discovery is further made that a thiol film on the  
13 gold terminals adheres to polyaniline nanofibers for securing a  
14 nanofiber polyaniline thin film to a gold conductor. Discovery  
15 is further made that polyaniline nanofibers, having diameters  
16 less than 500 nm and lengths less than 10  $\mu\text{m}$ , in a thin film  
17 have sufficient conductivity changes in response to dopants and  
18 dedopants to be suitable for use in chemical sensors. Discovery  
19 is also made that selective acids used during polymerization of  
20 the polyaniline nanofibers predetermine the resulting diameter  
21 of the nanofibers. In the preferred form, an acid and base  
22 chemical vapor sensor can be made using conventional gold  
23 sensor terminals covered by a polyaniline nanofiber thin film.

24  
25 In the preferred form, polyaniline nanofibers can be  
26 uniformly produced with predetermined diameter sized nanofibers  
27 having predetermined lengths in a normal distribution. During  
28 polymerization, a selected acid is used to efficiently

1 facilitate the polymerization process, which is selected to  
2 predetermine a normal distribution of diameters of the product  
3 polymer nanofibers. Each different diameter nanofiber has a  
4 resulting different chemical response, and hence, the  
5 polymerization process can be tailored to specific performances  
6 of the chemical sensors. These polyaniline nanofibers can then  
7 be used in a variety of chemical sensors, such as acids, bases,  
8 alcohols, volatile organic chemicals and reducing agents. The  
9 resulting thin film sensors made of the nanofibers have  
10 superior performance in both sensitivity and time response to a  
11 variety of gas vapors. Exemplar acids include hydrochloric  
12 acid, sulfuric acid, nitric acid, perchloric acid, and  
13 camphorsulfonic acid. Exemplar bases include ammonia and  
14 butylamine. Exemplar alcohols include methanol, ethanol, and  
15 propanol. Exemplar volatile organic chemicals include  
16 chloroform and nitromethane. Exemplar reducing agents include  
17 hydrazine.

18  
19 In the general form, polymer nanofibers can change  
20 physical properties such as conductivity, density,  
21 conformation, oxidation state, and optical absorption, among  
22 others, offering a wide variety of sensors for sensing various  
23 materials. Polyaniline nanofibers with uniform diameters have  
24 predetermined response characteristics. The polyaniline  
25 nanofibers can be made in bulk quantities through a facile  
26 aqueous and organic interfacial polymerization method at  
27 ambient conditions. The nanofibers have varying lengths within  
28 a normal distribution and form interconnected networks as a

1 thin film of polyaniline. In the general form, the invention is  
2 directed to a synthesis method for producing polymer nanofibers  
3 well suited for use in chemical sensors. In the preferred form,  
4 the method is suitable for bulk production of polyaniline  
5 nanofibers for use in acid and base chemical sensors. The  
6 synthesis method is preferably applied to organic monomers that  
7 can be linked into conducting polymers, such as polyaniline,  
8 polypyrrole, polythiophene and their derivatives. A template-  
9 free process using an aqueous polymerization bath provides a  
10 practical bulk synthetic method capable of producing bulk  
11 quantities of pure and uniform nanofibers with small  
12 predetermined diameters. The synthesis method is based on  
13 chemical oxidative polymerization of the monomers. The  
14 polymerization process is perfected in an immiscible, organic-  
15 aqueous, two-phase system. The synthetic method yields polymer  
16 nanofibers with nearly uniform reproducible diameters. These  
17 and other advantages will become more apparent from the  
18 following detailed description of the preferred embodiment.

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Brief Description of the Drawings

Figure 1A is a chemical diagram of doped polyaniline emeraldine salt.

Figure 1B is a chemical diagram of undoped polyaniline emeraldine base.

Figure 2 is a process flow of a method for synthesizing polyaniline nanofibers.

Figure 3 is a process flow of a method for forming an acid sensor.

Figure 4A is a graph of polyaniline nanofiber time response to an acid dopant.

Figure 4B is a graph of polyaniline nanofiber time response to a base dedopant.

Figure 5 is a process flow of a method for forming a polyaniline nanofiber precoated sensor.

Figure 6 is a block diagram of a polyaniline nanofiber precoated sensor.

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## Detailed Description of the Preferred Embodiment

An embodiment of the invention is described with reference to the figures using reference designations as shown in the figures. Referring to Figures 1A and 1B, monomers, such as aniline monomers can be linked together to form polyaniline. The polyaniline can be doped with an acid, such as hydrochloric acid HCl dopant, as shown in Figure 1A, and can be dedoped with a base, such as, ammonia  $\text{NH}_3$ .

Referring to Figures 1A, 1B, and 2, and more particularly to Figure 2, a seven-step method of synthesizing polyaniline nanofibers relies on a facile chemical process to produce high quality polyaniline nanofibers under ambient conditions using an aqueous-organic interfacial polymerization.

In step 1, a catalysis solution is first formed from water, an acid, and an oxidizer. The acid is preferably hydrochloric acid HCl, but other acids may be used, such as sulfuric acid  $\text{H}_2\text{SO}_4$ , nitric acid  $\text{HNO}_3$ , perchloric acid  $\text{HClO}_4$ , phosphoric acid  $\text{H}_3\text{PO}_4$ , acetic acid  $\text{CH}_3\text{COOH}$ , formic acid  $\text{HCOOH}$ , tartaric acid  $\text{C}_4\text{H}_6\text{O}_6$ , methanesulfonic acid  $\text{CH}_3\text{SO}_3$ , ethylsulfonic acid  $\text{C}_2\text{H}_5\text{SO}_3$ , 4-toluenesulfonic acid  $\text{C}_7\text{H}_8\text{SO}_3$ , and camphorsulfonic acid (CSA). The oxidizer is preferably ammonium peroxydisulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , but other oxidizers may be used, such as iron chloride  $\text{FeCl}_3$  and other peroxydisulfate derivatives such as  $\text{Na}_2\text{S}_2\text{O}_8$  and  $\text{K}_2\text{S}_2\text{O}_8$ . In step 2, a monomer solution is formed from a solution of a nonconducting monomer and an organic solvent.

1 In the preferred form, the monomer is aniline, but other  
2 carbon-based organic monomers can be used, such as pyrrole,  
3 thiophene, toluidine, anisidine and other derivatives of  
4 aniline such as methylaniline, ethylaniline, 2-alkoxyaniline,  
5 and 2,5 dialkoxyaniline monomers, for forming polyaniline,  
6 polypyrrole, polythiophene, polytoluidine, polyanisidine,  
7 polymethylaniline, polyethylaniline, poly2-alkoxyanilines and  
8 poly2,5-dialkoxyanilines respectively. The organic solvent is  
9 preferably carbon tetrachloride ( $\text{CCl}_4$ ), but other organic  
10 solvents may be used, such as benzene, toluene, chloroform,  
11 methylene chloride, xylene, hexane, diethylether,  
12 dichloromethane and carbon disulfide. In the preferred form,  
13 aniline monomers are dissolved in carbon tetrachloride ( $\text{CCl}_4$ ).  
14

15 In step 3, the monomer solution is disposed in a reaction  
16 vessel that can be scaled from small to large for increased  
17 batch production of bulk polymer nanofibers. In step 4, the  
18 catalysis solution is disposed nonturbulently into the reaction  
19 vessel and onto the monomer solution forming a bifurcated  
20 mixture having an aqueous organic reaction interface between  
21 the lower monomer solution and the upper floating catalysis  
22 solution. In step 5, a polymerization reaction occurs at the  
23 aqueous organic reaction interface creating conductive doped  
24 nanofiber polyaniline forming in the upper aqueous catalysis  
25 solution. The catalysis solution becomes a polymer solution  
26 comprising polymers of linked monomers from the monomer  
27 solution. As the catalysis solution becomes a polymer solution,  
28 the monomer solution is depleted of monomers and becomes an



1 organic solution. Aniline polymerizes at the interface between  
2 the bottom organic monomer solution containing dissolved  
3 aniline and the upper aqueous catalysis solution containing the  
4 oxidant and dopant. As the polymerization reaction proceeds,  
5 polyaniline nanofibers form across the interface, slowly  
6 diffusing and dispersing into the upper aqueous catalysis  
7 solution and eventually filling the upper aqueous solution with  
8 dissolved polyaniline nanofibers. At the same time, the color  
9 of the lower organic layer turns red-orange due to the  
10 formation of by-products, such as aniline oligomers. The  
11 nanofiber product in the upper organic solution is then  
12 collected and purified by conventional processes such as either  
13 dialysis or filtration, yielding a nanofiber product in the  
14 form of a water dispersion or a powder, respectively. Further  
15 washing or dialyzing with water yields pure, doped polyaniline,  
16 which can be dedoped by washing or dialyzing with a base, such  
17 as aqueous ammonia. High quality polyaniline nanofibers with  
18 dopants ranging from mineral acids to organic acids can be  
19 made. The synthesis is readily scalable and can be carried out  
20 at room temperature.

21  
22 In step 6, the polymer solution of polymers is separated  
23 from the organic solution. This may be accomplished by  
24 siphoning off the top floating polymer solution, and then  
25 disposing of the spent organic solution. In step 7, the polymer  
26 solution is purified into polyaniline nanofibers. The  
27 purification step 7 can be accomplished by conventional  
28 filtration or dialysis methods to effectively extract the

1 polymer nanofibers from the polymer solution. For example, the  
2 purification can be by dialysis of the colloidal suspension  
3 using standard commercially available dialysis membranes.  
4

5 The polymer nanofibers are preferably conducting polymer  
6 nanofibers having predetermined sizes, reactions, and  
7 sensitivities to predetermined chemical vapors. The nanofibers  
8 have nearly uniform predetermined diameters dependent upon the  
9 specific acid used in the catalysis solution. The acidic anion  
10 has a predetermined size, which when bound to the nanofiber  
11 polymer backbone, affect the overall diameter size of the  
12 nanofiber, having typical sizes mostly between 20 and 150 nm  
13 and less than 500 nm. For example, hydrochloric acid produces  
14 polyaniline nanofibers with a 30 nm diameter distribution, CSA  
15 acid produces polyaniline nanofibers with a 50 nm diameter  
16 distribution, and perchloric acid produces polyaniline  
17 nanofibers with a 120 nm diameter distribution, all with  
18 lengths varying from 500 nm to 5  $\mu$ m. In the general form, the  
19 nanofibers have diameters that are less than 500 nm and lengths  
20 less than 10  $\mu$ m.  
21

22 Gram scale beaker production to kilogram scale vat  
23 production can be used to synthesize various quantities of  
24 production polymer nanofibers. The nanofibers are typically  
25 twisted together forming an interlocking network or mesh of  
26 nanofibers. That is, the nanofibers tend to agglomerate into  
27 interconnected nanofiber networks, rather than bundles. Doping  
28 and dedoping does not affect the fibrillar morphology. As such,

1 the networks of nanofibers have improved sensitivities, are  
2 durable for repeated use, and are well suited for thin film  
3 deposition on sensor terminals. The nanofibers can then be thin  
4 film deposited onto conducting terminals on an insulating  
5 substrate to form a sensor.

6  
7 Referring to Figures 1A, 1B, 2, and 3, and more  
8 particularly to Figure 3, an acid chemical sensor can be made  
9 using polyaniline nanofibers when a method of forming an acid  
10 sensor having steps 8-13. In step 8, purified polyaniline  
11 nanofibers are disposed in a basic water solution for forming  
12 an undoped polyaniline nanofiber solution. Discovery is made  
13 that polyaniline nanofibers are stable in water, and can be  
14 rapidly dedoped in water using a basic solution. In step 9, the  
15 dedoped nanofiber polyaniline fibers are purified into a mass  
16 of dedoped nanofiber polyaniline. In step 10, the dedoped  
17 nanofiber polyaniline is disposed into water for forming a  
18 working solution.

19  
20 In step 11, the conducting terminals are formed on a  
21 sensor substrate. The sensor substrate can be made of an  
22 insulating material such as glass or quartz. The sensor  
23 terminals can be made of a conducting material such as  
24 semiconductors and conductors including gold, silver, platinum,  
25 polysilicon and doped photoresist. In step 12, the working  
26 solution is disposed onto sensor conducting terminals for  
27 coating the terminals with the nanofibers. This coating step  
28 can be accomplished by conventional coating methods such as

1 spin coating, drop coating, spray coating, and photolithography  
2 masked deposition coating. In step 13, the working solution is  
3 dried for coating a film of dedoped polyaniline nanofibers onto  
4 the sensor conducting terminals. The nanofibers will then react  
5 to the presence of various chemicals and solutions, such as an  
6 acid causing a change in conductivity that can be sensed at the  
7 sensor terminals.

8  
9 Referring to Figures 1A, 1B, 2, 3, 4A, and 4B, and more  
10 particularly to Figures 4A and 4B, polyaniline nanofibers  
11 exhibit conductivity changes when dedoped or doped polyaniline  
12 nanofibers are exposed to an acid or when doped polyaniline  
13 nanofibers are exposed to a base. In the exemplar case, when  
14 camphorsulfonic acid is used in the catalysis solution, the  
15 polyaniline nanofibers have camphorsulfonic acid molecules are  
16 tightly incorporated within the polyaniline during the in-situ  
17 polymerization of aniline. Dedoped polyaniline nanofibers can  
18 be obtained by dialyzing the camphorsulfonic acid doped  
19 polyaniline against 0.1 M ammonium hydroxide, which produces  
20 the emeraldine base form of polyaniline. Once the  
21 camphorsulfonic acid molecules are removed, thin-film sensors  
22 made of dedoped fibers respond to repeated doping and dedoping.  
23 The sensor performance of the nanofibers having a predetermined  
24 size diameter distribution, can be measured using a dedoped  
25 nanofiber emeraldine base thin film, such as a 2.5  $\mu\text{m}$  thick thin  
26 film as compared to a conventional dedoped thin film, such as a  
27 1  $\mu\text{m}$  thick thin film that can be deposited on an array of  
28 interdigitated gold electrodes. The sensor is exposed to an

1 acidic dopant, such as hydrochloric acid, for acidic doping,  
2 and, then exposed to a base, such as ammonia, for basic  
3 dedoping. The sensor, for example, may consist of fifty pairs  
4 of electrodes at  $4970 \times 20 \times 0.18 \mu\text{m}$  on a glass substrate with  
5 interdigitated gaps of  $10 \mu\text{m}$ . The polyaniline nanofiber sensors  
6 then exhibit a fast, predetermined reaction time during both  
7 doping for acid vapor detection and dedoping for basic vapor  
8 detection. The conducting polyaniline nanofibers possess fast  
9 predetermined doping and dedoping times that are suitable for  
10 sensor applications.

11  
12 The real time resistance changes of a dedoped film can be  
13 monitored using an electrometer upon exposure to an acid, such  
14 as 100 ppm of hydrochloric acid HCl, as shown in Figure 4A, and  
15 of a fully HCl doped film exposed to a base, such as 100 ppm of  
16 ammonia  $\text{NH}_3$ , as shown in Figure 4B. The resistance changes of a  
17 nanofiber emeraldine base thin film and conventional thin film  
18 upon exposure to 100 ppm HCl vapor and HCl doped films exposed  
19 to 100 ppm  $\text{NH}_3$  vapor are shown. The  $R/R_0$  ratio is the resistance  
20  $R$  normalized to the initial resistance  $R_0$  prior to gas exposure.  
21 The nanofiber thin film responds faster than a conventional  
22 film to both acid doping and base dedoping even though the  
23 nanofiber film is more than twice as thick. This is due to the  
24 small, predetermined diameter size of the nanofibers that  
25 provides a high surface area within the film that can be  
26 rapidly accessed by the gas vapors. Also, the small,  
27 predetermined diameters of the fibers allow gas molecules to  
28 diffuse in and out of the fibers in a much shorter

1 predetermined amount of time. This also leads to a much greater  
2 extent of doping or dedoping over short times for the nanofiber  
3 films.

4  
5 Films of doped nanofiber and conventional polyaniline can  
6 be measured and compared in response to exposure to alcohol  
7 vapors, such as methanol, ethanol, and propanol, or to water  
8 vapor. The mechanism of response in the case alcohol or water  
9 exposure is not doping or dedoping but rather conformational  
10 changes of the polymer film. The conformational changes produce  
11 a resulting change in conductivity for use as an alcohol or  
12 water vapor sensor. Again, the nanofiber sensor has a greater  
13 response with a faster response time. In the case of volatile  
14 organic chemicals, the response mechanism is swelling of the  
15 polymer both in bulk film and in nanofiber forms. The swelling  
16 also causes a resulting change in electrical conductivity,  
17 which can be used to sense the organic vapor. Reducing agents  
18 such as hydrazine react with polyaniline nanofibers to cause a  
19 change in oxidation state and a corresponding change in  
20 electrical conductivity and can be used to sense hydrazine.  
21 The nanofibers can also react with chemical vapors with a  
22 change in optical absorption qualities that can be detected  
23 using coated optical detectors in the chemical sensors. In all  
24 cases, the nanofiber films have improved sensor performance in  
25 both sensitivity magnitude and time response as compared to  
26 conventional bulk films for a range of analytes.

1 Referring to Figure 5, an enhanced sensor can be made by  
2 precoating the gold terminal of a sensor with polyaniline prior  
3 to a thin film in a method described in steps 14 through 24.  
4 In step 14, conducting gold terminals are disposed on a sensor  
5 substrate. In step 15, the gold terminals are exposed to 4-  
6 Amino Thiophenol (4-ATP) for forming a thiol RSH surface layer  
7 on the gold terminals. In step 16, the catalysis solution is  
8 formed of water, acid, and oxidizer. In step 17, the monomer  
9 solution is formed of the monomer and an organic solvent. In  
10 step 18, the monomer solution is disposed in a reaction vessel.  
11 In step 19, the sensor substrate is submerged in the vessel  
12 with the gold terminals positioned at the surface of the  
13 monomer solution. In step 20, catalysis solution is disposed  
14 onto the monomer solution forming an aqueous organic reaction  
15 interface flush with the gold terminals. A precoating of  
16 polyaniline nanofibers is formed over upon the thiol RSH  
17 surface layer while polyaniline nanofibers are also formed at  
18 the interface and dispersed into the catalysis solution. In  
19 step 21, the polymerization reaction is continued at the  
20 aqueous organic reaction interface creating conductive, doped  
21 polyaniline nanofibers that precoat the gold terminals while  
22 creating conductive, doped nanofiber polyaniline in the  
23 catalysis solution then becoming a polymer solution as the  
24 monomer solution becomes an organic solution. Alternatively,  
25 the polymerization reaction can also be continued to create a  
26 polyaniline nanofiber film that results in a conducting  
27 nanofiber film that spans electrodes to provide a complete  
28 chemical sensor after washing of the resulting film. In step

22, the polymer solution is separated from the organic solution, while the precoated substrate is removed from the vessel. In step 23, the polymer solution is purified into polyaniline nanofibers. In step 24, a film of the polyaniline nanofibers is disposed over the precoated gold terminals for forming a precoated sensor as shown in Figure 6.

Referring to Figure 6, a polyaniline nanofiber precoated acid sensor includes the insulating substrate, at least two gold terminals, including a positive gold terminal and a negative gold terminal, upon both of which is disposed a thiol (RSH) film and a polyaniline precoat. Over the precoated gold terminals is disposed the thin film of polyaniline nanofibers. The precoating offers enhanced adherence and contact conductivity between the gold terminals and the polyaniline film. When the polyaniline film is exposed to a chemical vapor, the conductivity of the polyaniline film changes producing changes in resistivity that would then produce a change in electrical current as measured by a current meter that is connected in series with a DC power source that is in turn connected across the positive and negative gold terminals.

Referring to all of the figures, the synthesis method is based on the chemical oxidative polymerization of a monomer, such as aniline, in a strongly acidic catalysis solution having an acid component, such as camphorsulfonic acid, and an oxidant, such as ammonium peroxydisulfate. The polymerization is performed in an immiscible organic-aqueous biphasic system,



1 in order to separate the by-products, including inorganic  
2 salts, and oligomers, according to solubility in the organic  
3 and aqueous phases. In an exemplar synthetic process, aniline  
4 is dissolved in an organic solvent, such as  $\text{CCl}_4$ , benzene,  
5 toluene, or  $\text{CS}_2$  while ammonium peroxydisulfate is dissolved in  
6 water with camphorsulfonic acid. The two solutions are  
7 transferred into a reaction polymerization vessel for  
8 generating an interface between the two solutions. After a  
9 short period, such as a few minutes, green polyaniline forms at  
10 the interface and then gradually diffuses and disperses into  
11 the aqueous phase of the catalysis solution. After an extended  
12 period, such as several hours, the entire water phase is  
13 homogeneously filled with dark green polyaniline, while the  
14 lower organic layer appears red-orange, due to the formation of  
15 aniline oligomers. The aqueous phase is then collected and the  
16 by-products are removed by dialysis against deionized water,  
17 using for example, tubing with a 12K to 14K cutoff. When a  
18 deionized water bath reaches a pH of 7, a 10- $\mu\text{l}$  suspension is  
19 diluted with 1 ml of deionized water. Dedoped polyaniline can  
20 then be obtained by dialysis using 0.1 M ammonium hydroxide and  
21 then deionized water. The synthetic method produces yields  
22 ranging from six to ten weight percent of nanofibers. Thin film  
23 sensors made of the polyaniline nanofibers have superior  
24 performance in both sensitivity and time response to a variety  
25 of gas vapors including acids such as hydrochloric,  
26 hydrofluoric, sulfuric, and nitric, bases such as ammonia and  
27 butylamine, and alcohols such as methanol, ethanol, and  
28 propanol. Thin film sensors made of the polyaniline nanofibers

1 are also sensitive to some volatile organics such as chloroform  
2 and nitromethane, and to redox agents such as hydrazine.

3  
4 The aqueous and organic interfacial synthesis of  
5 polyaniline nanofibers has several advantages. Both the  
6 synthesis and purification steps are template free. Uniform  
7 nanofibers are obtained in high yields. The synthesis method is  
8 scalable and reproducible with predetermined reactions and  
9 response times. Multiple syntheses performed from millimolar to  
10 molar quantities produce nanofibers of the same morphology,  
11 size distribution and uniformity. The nanofibers are readily  
12 dispersed in water, which facilitates environmentally friendly  
13 processing and biological applications. The nanofiber sensors  
14 have shorter doping and dedoping times with greater response to  
15 acidic and basic gases. The nanofiber sensors have a faster and  
16 larger response to alcohol vapors and react to some volatile  
17 organics and redox agents. Chemical sensors made from the  
18 nanofibers respond with larger magnitudes and faster response  
19 times to a wide range of analytes, and are well suited for  
20 chemical sensor applications.

21  
22 The present invention is generally directed to a synthesis  
23 method for forming polymer nanofibers. When the polymer  
24 nanofibers are conductive, the resulting thin film can be used  
25 in a chemical sensor. Conducting polymer nanofibers include  
26 polyaniline nanofibers, polypyrrole nanofibers, and  
27 polythiophene nanofibers all of which can be used in chemical  
28 sensors. The method relies on the use of a monomer solution

1 comprising an organic monomer and an organic solvent, and the  
2 use of a catalysis solution comprising an acid and an oxidizer,  
3 for producing at an aqueous and organic interfacial interface  
4 polymer nanofibers that preferably react to vapor exposures for  
5 suitable use in chemical sensors. Various monomers, solvents,  
6 oxidizers, and acids can be used as alternatives,  
7 modifications, and improvements to the preferred forms. Those  
8 skilled in the art can make enhancements, improvements, and  
9 modifications to the invention, and these enhancements,  
10 improvements, and modifications may nonetheless fall within the  
11 spirit and scope of the following claims.

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1 What is claimed is:

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3 1. A sensor for sensing the presence of a chemical vapor, the  
4 sensor adapted for interconnecting to an electrical monitor for  
5 measuring a reaction of the sensor to the chemical vapor, the  
6 sensor comprising,

7 a positive terminal, the positive terminal being conductive,

8 a negative terminal, the negative terminal being conductive,

9 the terminals adapted for interconnection to the electrical  
10 monitor, and

11 a film of organic conductive polymer nanofibers extending  
12 between the positive and negative terminal for producing a  
13 change in conductivity between the positive terminal and the  
14 negative terminal as monitored by the electrical monitor when  
15 the film is exposed to the chemical vapor.

16

17 2. The sensor of claim 1 wherein,

18 the positive terminal and the negative terminal are made of  
19 gold.

20

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22 3. The sensor of claim 1 wherein the positive terminal and the  
23 negative terminal are made of gold and the conducting polymer  
24 is polyaniline, the sensor further comprising,

25 a thiol surface layer disposed between the terminals and the  
26 film.

27

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1 4. The sensor of claim 1 wherein,  
2 the polymer nanofibers are selected from the group  
3 consisting of polyaniline nanofibers, polypyrrole nanofibers,  
4 polythiophene nanofibers, polytoluidine nanofibers,  
5 polyanisidine nanofibers, polymethylaniline nanofibers,  
6 polyethylaniline nanofibers, poly2-alkoxyanilines nanofibers  
7 and poly2,5-dialkoxyanilines nanofibers.

8  
9 5. The sensor of claim 1 wherein,  
10 the polymer nanofibers are polyaniline nanofibers, and  
11 the chemical vapor is selected from the group consisting of  
12 an acid vapor and a basic vapor.

13  
14 6. The sensor of claim 1 wherein,  
15 the polymer nanofibers have diameters less than 500 nm and  
16 lengths less than 10  $\mu\text{m}$ .

17  
18 7. The sensor of claim 1 wherein,  
19 the polymer nanofibers are polyaniline nanofibers having  
20 diameters less than 500 nm and lengths less than 10  $\mu\text{m}$ .

21  
22 8. The sensor of claim 1 wherein,  
23 the polymer nanofibers are polyaniline nanofibers having  
24 distributed diameters of 50 nm.

25  
26 9. The sensor of claim 1 wherein,  
27 the polymer nanofibers are polyaniline nanofibers having  
28 distributed diameters of 30 nm.

1 10. The sensor of claim 1 wherein,  
2 the polymer nanofibers are polyaniline nanofibers having  
3 distributed diameters of 120 nm.

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Abstract of the Disclosure

Polymer nanofibers, such as polyaniline nanofibers, with uniform diameters less than 500 nm can be made in bulk quantities through a facile aqueous and organic interfacial polymerization method at ambient conditions. The nanofibers have lengths varying from 500 nm to 10  $\mu\text{m}$  and form interconnected networks in a thin film. Thin film nanofiber sensors can be made of the polyaniline nanofibers having superior performance in both sensitivity and time response to a variety of gas vapors including, acids, bases, redox active vapors, alcohols and volatile organic chemicals.

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